



The concept of pillaring in clays, already defined by three criteria¹, needs to be partly modified: i) intercalation, generally by cationic exchange in the interlamellar space, of a cationic pillar which increases the interlayer distance ($d_{001} = 16.6 \text{ \AA}$) by at least 7 \AA to yield a structure with properties challenging those of zeolites in their applications, ii) a free height - not always correctly evaluated by porosity measurements² - important in a number of applications, iii) irreversibility under specific conditions (from 200°C up to $700\text{--}800^\circ\text{C}$), under anhydrous or hydrothermal atmospheres, or pH variations (in acidic or basic solutions).

PILCs have been extensively studied since 1974 as a function of i) the nature of the clays, ii) the nature of the pillars, iii) the conditions of pillaring, iv) the nature of the applications³, but syntheses of mixed PILCs are sparse, and to our knowledge, there is as yet no proof that mixed pillars are present when two cationic species are intercalated simultaneously.

Our studies of pillaring of montmorillonite and synthetic hectorite (laponite) by Al and Fe oxides, started 10 years ago⁴, showed for the first time that a part of the Keggin cation Al^{3+} was substituted by Fe atoms⁵⁻⁷. These results have recently been confirmed by a paper⁸ concluding that Fe^{3+} is incorporated in the Al_{13} Keggin structure at Fe/Al ratios < 0.5 (solutions of $AlCl_3$ and $FeCl_3$ were added to a clay suspension in appropriate conditions. In practice, it may be more useful to use more concentrated clay suspensions^{3,9}). The choice of iron-free laponite (with a low aluminium content) and of the reference state allowed us to use chemical analysis without ambiguity and with great accuracy. The iron is preferentially retained by the clay¹⁰ in contact with the two

metal ions. XRD and BET surface area measurements confirm pillaring of laponite. Many conclusions can be drawn from analytical NMR and H_2 TPR results:

- 1) For the Al-rich samples (molar ratio 5 to 30% Fe^{3+} in initial solutions), mixed pillared clays are obtained with up to 25% isomorphous replacement of Al by Fe in which the iron is not reducible, whereas the out-of-pillars iron retained by the clay is reducible.
- 2) For the Fe-rich samples (50 and 100% Fe), all the iron is reducible but at two different temperatures. The structure of the iron pillars (with d_{001} about 22 \AA) is certainly different, as described elsewhere¹¹, from that of the pure Al_{13} pillars. The great amount of residual iron shows up after H_2 reduction as large important particles of metallic iron out of the interlamellar space of the clay.

The mixed Al-Fe PILCs present original catalytic properties different from those of conventional iron catalysts^{5-6,12-13} in the CO, H_2 reaction. The activities are significantly enhanced when the total iron content increases and are very stable at high temperature. The presence of mixed pillars results in high proportion of olefin formation and shape selectivity, the distribution of hydrocarbons does not follow the Schulz-Flory law. This selectivity deviation disappears for the sample at the limit of isomorphic substitution.

All these results were obtained in collaboration with the laboratory of catalysis (Poitiers). They are formalized by the publication of two theses^{14,15} and two French patents¹⁶ taken out with Gaz De France.